Enhanced Trichloroethene Desorption from Long-Term Contaminated Soil Using Triton X-100 and pH Increases

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Laboratory batch and column experiments were conducted to study the effect of relatively low concentrations of Triton X-100 and pH increases on trichloroethene (TCE) desorption from field-contaminated soil to water. TCE desorption from the contaminated soil could not be described by a model that assumes a localized equilibrium between the aqueous- and sorbed-phase concentrations of TCE. A kinetic desorption model, the multi-site model with a γ-distribution of rate constants, was used to interpret the data and to determine the mass-transfer coefficients. In both batch and column experiments, the multi-site model performed well in simulating TCE desorption. In laboratory batch and column experiments, the addition of Triton X-100 (at concentrations close to critical micelle concentration) to the soil-water system increased the rate of TCE desorption from the soil at early times, although only by a small amount. Similar results were obtained by increasing the solution pH from 7 to 10. In experiments with Triton X-100, the mean mass-transfer coefficient increased by 11.2% in batch tests and 16.5% in column tests relative to experiments without Triton X-100. The mean mass-transfer coefficient increase caused by increasing pH from 7 to 10 was 53% in batch tests and 7% in column tests.

Introduction

Across the nation, anthropogenic activities have resulted in the contamination of soil and groundwater by chlorinated solvents, petroleum hydrocarbons, pesticides, and other hazardous organic chemicals. Over the past 20 yr, pump-and-treat has been the most common method to remediate contaminated groundwater (*1*); experience with the pump-and-treat systems has revealed that the rate of extraction of contaminants is often less than predicted. Reasons for the inefficiency of these systems include the presence of non-aqueous-phase liquids (*2, 3*), subsurface heterogeneities (*4*), and rate-limited desorption of the contaminants from soil to water (*5−15*). This latter problem of slow pollutant desorption from long-term field-contaminated soil is the focus of this paper.

Several different processes have been theorized to cause this sorption-related non-equilibrium. It may result from chemical non-equilibrium (e.g., non-equilibrium associated with chemisorption), from intraparticle diffusion, or from intraorganic matter diffusion. For many nonpolar organic compounds such as trichloroethene (TCE), chemisorption does not appear to be a significant sorption mechanism (*5, 16*). On the other hand, partition of nonpolar organic compounds from water into soil organic matter by forces common to solution is generally believed to be the predominant sorption mechanism (*17*). Thus, diffusive mass-transport limitations, which include intraparticle diffusion and/or intraorganic matter diffusion, are primarily responsible for sorption non-equilibrium. Intraparticle diffusion is the diffusion of a solute through the micropores of mineral particles or aggregates followed by equilibrium sorption with the pore walls (*18, 19*). Intraorganic matter diffusion is the diffusion of a solute through the soil organic matrix; several studies have suggested that intraorganic matter diffusion may be the primary cause for non-equilibrium sorption in soil−water systems (*9, 16, 20, 21*).

For intraorganic matter diffusion, soil organic matter can be envisioned as a three-dimensional matrix of polymer chains with a relatively open, flexible structure (*16*). The diffusion of small solutes (benzene, TCE, etc.) in concentrated polymeric solutions is generally believed to be caused by the tortuous movement of the solute through the polymer matrix (*22*). The rate of diffusion is then controlled in part by the volume of the polymer matrix not occupied by the polymer molecules themselves (*23*). When the concentration of a solvent in a polymer is increased, the polymer matrix must undergo configurational changes that "swell" or expand the organic polymer medium. The resulting diffusion rate of a small solute molecule in the polymer solution can thereby be increased (*24, 25*). The magnitude of the diffusion coefficient of small solutes in concentrated polymers approaches the values of diffusion coefficients measured for solid media and have been reported to be smaller than 10^{-8} cm²/s (*24*).

One of the processes that may contribute to the slow desorption of solutes from soil organic matter and explain the observation that the rate of desorption varies inversely with the time of exposure to contamination is conformational changes in the soil organic matter over time. Over long time periods, changes in water pH, ionic strength, temperature, etc. may cause rearrangement of the alkyl and aryl functional groups in soil organic matter (*26*); which in turn may cause some fraction of the sorbed solute to be "trapped" as diffusional paths are blocked.

Regardless of the cause of slow solute desorption from soil, it is apparent that changes in water chemistry that result in the "swelling" of soil organic matter can potentially cause an increase in the rate of solute mass transfer from soil to water by reducing the diffusional tortuosity of the soil organic matter. A recent study has investigated the effect of surface-active agents (surfactants) on the rate of TCE desorption from laboratory-contaminated soil (*9*). This study reported that the nonionic surfactant Triton X-100 increases the mass-transfer coefficient for organic solute desorption from soil contaminated with TCE. It was hypothesized that the surfactants reduce the water−soil−organic matter interfacial tension and cause swelling of the soil organic matter. This in turn decreases diffusional resistances and increases the rate of solute desorption. In this study, we extend these experiments to the more difficult task of using a nonionic surfactant to increase the rate of TCE desorption from a long-term field-contaminated soil collected from Picatinny Arsenal, NJ. In addition, the effect of solution pH on the rate of TCE desorption from the field soil is examined. The multi-site kinetic sorption model was applied to desorption data from batch and column experiments, and the ability of the model to accurately describe the data is discussed.

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Model Development

Nonpolar hydrophobic organic compounds (HOCs) such as TCE are assumed to sorb and desorb by intraorganic matter diffusion. This diffusive transport may be represented approximately by a first-order rate equation. The mass transfer relation is given as

$$dS/dt = -k(S - K_{oc} f_{oc} C) = -k(S - K_d C) \tag{1}$$

where S is the sorbed TCE concentration (M/M), C is the aqueous TCE concentration (M/L^3), k is the mass-transfer rate constant ($1/T$), K_{oc} is the organic carbon-normalized sorption coefficient (L^3/M), f_{oc} is the mass-fractional soil organic carbon content, and K_d ($= K_{oc} f_{oc}$) is the equilibrium sorption coefficient (L^3/M). The term ($S - K_d C$) represents the concentration gradient. The multi-site model incorporating such a first-order mass transfer equation is examined here.

Multi-Site Model. It is widely recognized that natural soil is heterogeneous. Therefore, mass transfer may not be adequately described by one rate constant. Instead the sorption sites can be divided into many sites, each having a unique sorption mass-transfer rate constant. This sorption accounting for multiple kinetic sites is the multi-site model; this model is also often referred to as the multi-compartment model or distributed-site model. Following Connaughton et al. (28) and Culver et al. (15), we postulate a γ-density function to model a continuum of desorption rate constants. The density function is given by

$$f(k) = \beta^{\alpha} k^{\alpha-1} \exp(-\beta k)/\Gamma(\alpha) \tag{2}$$

where $f(k)$ is the likelihood that the solute molecule is in a compartment with desorption rate constant k, Γ is the γ-function, $1/\beta$ is the scale parameter, and α is the shape parameter. The γ-density function has a mean of α/β, a standard deviation of $(\alpha)^{1/2}/\beta$, and a coefficient of variation (standard deviation relative to the mean) of $\alpha^{-1/2}$. The γ-density function, with only two parameters α and β, is a convenient and flexible model to represent the distribution of sorption rate constants.

A one-dimensional, finite difference model incorporating multi-site sorption kinetics (15) is used to analyze and fit the column data. This model was also adapted to solve for a zero-dimensional, zero-velocity batch experiment. The governing equations incorporating the multi-site sorption column model are as follows:

$$\frac{\partial C}{\partial t} + \frac{\rho}{\theta}\frac{\partial S}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} \tag{3}$$

$$\frac{\partial S}{\partial t} = \sum_{\kappa=1}^{NK} k_{\kappa}[K_d C - S_{\kappa}] \tag{4}$$

where v is the linear velocity (L/T), ρ is the bulk density (M/L^3), θ is the moisture content or porosity, the subscript κ represents the κth sorption site, NK is the number of sites, S_{κ} is the solute concentration in the soil due to site κ, and S is the total solute concentration in the soil due to all the kinetic sites. NK discrete sites are used to represent the continuous distribution of sites, and each site occupies 1/NK fraction of the soil. The representative mass transfer coefficient, k_{κ}, for each of the sites is obtained from a γ-probability density function (15). The initial conditions for each of the soil sites is obtained by equally distributing the total measured soil–TCE concentration among the soil sorption sites.

Materials and Methods

Hexane, methanol, and TCE were obtained from Aldrich and Sigma Chemical Co. Triton X-100 [$C_6H_{17}C_6H_4O(CH_2CH_2O)_{9.5}H$]

is a nonionic, heterogeneous octylphenol ethoxylate surfactant and was obtained from Aldrich Chemical Co. The average molecular weight is 628. From laboratory measurement of surface tension at various concentrations of Triton X-100, the critical micelle concentration (cmc) was found to be 130 mg/L.

Soil used in this investigation was a composite of soil samples collected from several locations from the TCE-contaminated water table aquifer at Picatinny Arsenal in Morris County, NJ. Groundwater and soil at the site have been contaminated for more than 20 yr. Details of the site hydrogeology and contamination history are given elsewhere (29). The soil is predominantly a fine-to-medium sand. For laboratory experiments, some of the soil was collected from areas with a high peat content. The organic content of the composited soil is 1.04%. The soil was air-dried at room temperature for 24–72 h prior to use in experiments. This allowed accurate weighing of the soil and better handling during sieving and filling of the soil columns. The soil was air-dried at room temperature for 72 h prior to use in all batch experiments. Later, for the column-study phase of the laboratory experiments, we found that 24 h of drying was enough to improve soil handling and to remove most of the free water; therefore, the soil was air-dried at room temperature for 24 h prior to use in all column experiments. Koller et al. (30) observed that air-drying contaminated soil from Picatinny Arsenal had a negligible effect on the sorbed TCE concentration.

A pH 4 buffer solution was prepared using 4.48 g of potassium hydrogen phthalate [2-$(HO_2C)C_6H_4CO_2K$]/L of deionized organic-free water. A pH 7 buffer solution was prepared using 0.9 g of potassium phosphate dibasic (K_2-HPO_4) and 1.01 g of potassium monobasic phosphate (KH_2-PO_4)/L of water. A pH 10 buffer was prepared using 0.317 g of sodium bicarbonate ($NaHCO_3$) and 0.806 g of sodium carbonate (Na_2CO_3)/L of water. All pH buffer solutions had an ionic strength of approximately 0.02 M.

Batch Desorption Experiments. Three types of batch desorption experiments were conducted: (i) desorption into water at pH 7, (ii) desorption into water buffered at pH 10, and (iii) desorption into water at pH 7 and with an equilibrium aqueous Triton X-100 concentration of 94 mg/L. Each desorption experiment consists of nine duplicate 15-mL glass centrifuge tubes with Teflon-lined caps containing 6 g of field-contaminated soil, 11 mL of water, and the appropriate pH buffer or Triton X-100 mass. The reactors were shaken on a rotary shaker (Boekel Orbitron Rotator Model 260200) at room temperature until sampling. At various time intervals, duplicate centrifuge tubes were sacrificed for analysis. The tubes were centrifuged at 1500g for 10 min (Dupont Sorvall, RT 6000 B Centrifuge). Five milliliters of supernatant was contacted with 1 mL of hexane to extract TCE. The hexane extract was analyzed by gas chromatography (Perkin Elmer Autosystem) with an electron-capture detector. The gas chromatograph is controlled by a Model 1022 GC Plus integrator that stores and processes the chromatographic data.

To quantify the initial sorbed TCE concentration on the soil, quadruplicate samples of soil were air-dried at room temperature for 24 h, extracted into methanol for 48 h at 75 °C, concentrated in hexane, and analyzed by gas chromatography with an electron-capture detector (31, 10). The average initial TCE concentration on the soil was 1100 μg/kg, and the standard deviation was 105 μg/kg.

A batch equilibrium procedure was used to determine the equilibrium distribution coefficient of TCE between water and soil. Clean soil (6.0 g) and water or other aqueous solutions (12 mL) were added to 15-mL centrifuge tubes. Prior to use in these equilibrium experiments, TCE in the soil was removed by heating the soil sample for 48 h at 105 °C; the soil was analyzed after incubation, and no TCE was detected. Different amounts of TCE were injected into each vial. After

TABLE 1. Partition Coefficients, K_d, (and Standard Errors) for Trichloroethene Sorption to Soil from Different Aqueous Solutions following a 72-h Equilibration Period

solution	K_d (L/kg)	solution	K_d (L/kg)
deionized H_2O	0.69 ± 0.02	Triton X-100 (1050 mg/L)	0.84 ± 0.08
Triton X-100 (58 mg/L)	0.71 ± 0.08	Triton X-100 (1850 mg/L)	0.78 ± 0.08
Triton X-100 (105 mg/L)	0.78 ± 0.08	pH 4	0.77 ± 0.015
Triton X-100 (310 mg/L)	0.86 ± 0.01	pH 7	0.72 ± 0.02
Triton X-100 (480 mg/L)	0.90 ± 0.08	pH 10	0.68 ± 0.022

3 d of shaking at 15 °C, the aqueous TCE concentration was measured. The partition coefficients were obtained by fitting a linear isotherm model to the data.

Column Experiments. Laboratory column studies were performed using 2.54 cm diameter and 30 cm long glass columns packed with field soil. The columns were fitted on both ends with fine stainless steel wire mesh of 1 μm spacing to prevent elution of soil fines. Three sets of columns (each consisting of two columns) were set up, and different solutions were flowed through them. Surfactant (Triton X-100) at 300 mg/L, deionized organic-free water (buffered at pH 7), and pH 10 buffer solution, respectively, were pumped through each set of two columns. A peristaltic pump (Manostat cassette pump) was used to pump aqueous solutions at a constant rate through the columns. To minimize sorption of TCE to the walls of the tubing or columns, only Teflon tubing and glass columns were used. The effluent concentrations (TCE and surfactant) were measured at various time intervals for approximately 70 pore volumes of flow, after which the final soil concentration was measured by hot methanol extraction as described earlier. A Br$^-$ tracer test was performed in all the columns. The breakthrough curve was fitted using the conventional breakthrough curve for an advective−dispersive system to estimate the linear velocity of water and the dispersion coefficient.

Effluent samples from the column were collected in 5-mL air-tight flow-through tubes. These glass sampling tubes were sealed at both ends with Supelco Mininert valves, and the flow of effluent flowed through the tubes via a pair of syringe needles. The TCE concentration in the effluent was measured by extracting 4 mL of sample with 1 mL of hexane. The hexane extract was analyzed by gas chromatography. Triton X-100 was measured using a calibrated Fischer Scientific surface tensiometer 20.

Results and Discussion

Partition Coefficients. The TCE partition coefficients (K_d) on soil in contact with different aqueous phases are given in Table 1. The K_d value for soil-DI water system was found to be 0.69 L/kg. This corresponds to an organic carbon-normalized sorption coefficient (K_{oc}) of 66. The K_d values varied with Triton X-100 concentration, increasing from 0.69 L/kg at 0 mg/L Triton X-100 concentration to 0.89 L/kg at 480 mg/L Triton X-100 concentration and then decreasing to 0.78 at 1850 mg/L. The initial increase of K_d results from an increase in soil organic matter contributed by the sorption of Triton X-100 onto the soil. However, above aqueous-phase Triton X-100 concentrations of 480 mg/L, aqueous micellar pseudophase (cmc = 130 mg/L) forms, which increases the apparent aqueous-phase solubility of TCE resulting in a decrease of K_d. This effect, using different solutes, was first described by Edwards et al. (*32*) and later by Sun et al. (*33*).

In the case of pH changes, the K_d was observed to vary inversely with pH. Higher pH causes swelling of the soil organic matter due to like-charge repulsion, and the resultant hydration of the organic matter increases its polarity and decreases its solvency for TCE—hence lowering K_d (*34*). Kan and Tomson (*35*) also noted the pH dependence of sorption with naphthalene in soil columns and found decreased sorption with pH rise. The K_d is greater with pH 7 buffer than
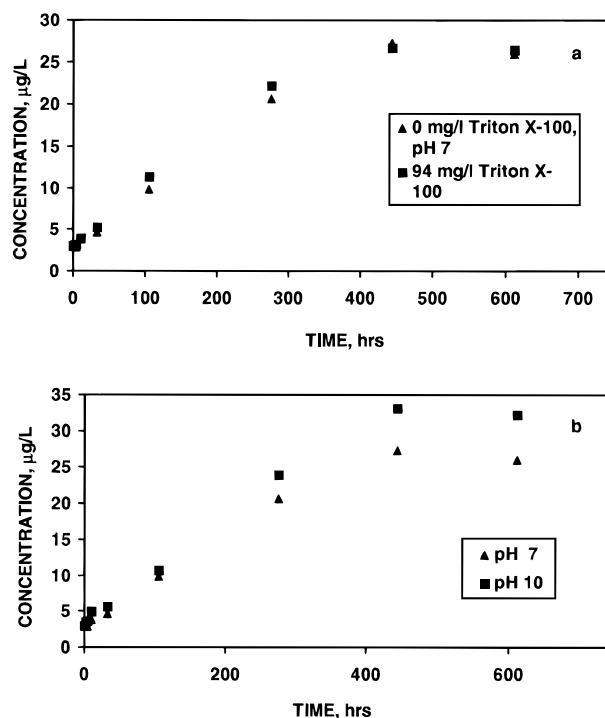

FIGURE 1. Aqueous concentration of TCE versus time in batch reactors at (a) equilibrium aqueous Triton X-100 concentrations of 0 and 94 mg/L and (b) pH 7 and pH 10.

with deionized water as the aqueous phase (Table 1). The pH of the deionized water−soil mixture was approximately 7.3; this difference in pH may explain to some extent the variation in K_d values in these two systems.

Equation 1, the mass-transfer rate expression, suggests that the value of K_d affects the concentration gradient, which in turn affects the sorption rate. In the case of desorption, lower K_d increases the mass-transfer rate and higher K_d decreases the mass-transfer rate. Therefore, it can be expected that higher pH and higher Triton X-100 concentrations (up to about 480 mg/L), because of their effect on K_d, will increase and decrease the desorption concentration gradient, respectively.

Batch Results. A comparison of TCE concentrations versus time in batch reactors with 0 mg/L (at pH 7) and 94 mg/L Triton X-100 are shown in Figure 1a. At times less than 450 h, the aqueous TCE concentration is higher for the 94 mg/L Triton X-100 solution than for the 0 mg/L Triton X-100 solution. This indicates that Triton X-100 increases the desorption rate at the early period of the experiment. After about 450 h, the aqueous TCE concentration in all the reactors was similar. The rate of desorption seems to have slowed at this stage. Considering that only about 6% of equilibrium desorption (calculated from the aqueous-phase TCE concentration, the soil-phase TCE concentration, and the assumption that equilibrium is defined based on the isotherm data of Table 1) has occurred, slow desorption can be expected to continue for a much longer time. With regard to the influence of pH, plots of aqueous TCE concentration versus

TABLE 2. Mean Mass-Transfer Coefficients and Coefficient of Variation ($\alpha^{-1/2}$) for TCE Desorption from Soil in Batch Reactors

influent solution	0 mg/L Triton X-100, pH 7	94 mg/L Triton X-100	pH 10
mass-transfer coefficient (h^{-1})	4.73×10^{-4}	6.02×10^{-4}	4.00×10^{-4}
$\alpha^{-1/2}$	8.055	8.45	6.36
error[a]	0.0133	0.0122	0.0139
mass-transfer coefficient (h^{-1})	4.73×10^{-4}	5.26×10^{-4}	7.25×10^{-4}
$\alpha^{-1/2}$	8.055	8.055	8.055
error	0.0133	0.0124	0.01733

[a] Error = [(sum of squares of deviation)/(sum of squares of data values)]$^{0.5}$.

time at pH 7 and pH 10 show that the rate of desorption increases at higher pH (Figure 1b).

The multi-site model is used to quantify the increase of the mass-transfer constant due to Triton X-100 and increased pH (Table 2). In the batch reactors with no surfactant, the coefficient of variation (CV) is 8.055, and the mean mass-transfer coefficient is 4.73×10^{-4} h^{-1}. These results show that the presence of surfactant increases the coefficient of variation slightly but significantly increases the mean mass-transfer coefficient to 6.02×10^{-4} h^{-1}. At the high pH conditions, the CV decreases to 6.36 and so does the mean mass-transfer coefficient (from 4.73×10^{-4} h^{-1} to 4.00×10^{-4} h^{-1}). The change in CV indicates that the distribution of the mass-transfer constant changes with solution pH and surfactant concentration. In the case of surfactant, however, the change in CV is relatively small. Since CV and the mean mass-transfer coefficient together affect the overall mass transfer of TCE from the soil to the water, it is difficult to clearly compare the influence of pH and surfactant from these two values.

So, for the purpose of making such comparison, a set of model runs in which the CV is kept constant are also presented in Table 2. The shape of the γ-density function, which represents the relative distribution of the rate constants among the compartments, is kept constant in all the tests by keeping the coefficient of variation, $\alpha^{-1/2}$, constant. The value of $\alpha^{-1/2}$ (8.055) from the batch reactor with 0 mg/L Triton X-100 and pH 7 is used to represent the CV of the rate constant distribution in all the batch reactors. This way, we assume that the relative distribution of the sites or the shape of the γ-density function is unchanging and only the magnitude of the mean rate coefficient is affected by the different solutions contacting the soil. As can be seen from the reported errors in Table 2, the model fits were only slightly worse than for the case where both CV and the mean mass-transfer constant were allowed to vary. Comparing directly the mean mass-transfer constants for the case of constant CV, Table 2 shows that the Triton X-100 solution caused an increase of the mean rate coefficient from 4.73×10^{-4} h^{-1} to 5.26×10^{-4} h^{-1} (11.2% increase). A change in pH from 7 to 10 caused the mean rate coefficient to increase to 7.25×10^{-4} h^{-1} (53% increase).

Column Results. The values of column flow and soil parameters are presented in Table 3. The K_d values used in modeling each of the columns are listed. Dispersion coefficient and velocity data obtained from bromide tracer tests show variation between columns, probably due to the difference in packing of soil among the columns. The sorbed TCE concentrations at the end of the experiment and their standard errors are also listed.

The effluent concentrations for columns with water and for the columns with Triton X-100 are plotted against pore volumes in Figure 2a. The effluent concentrations for columns with water and for the columns with pH 10 buffer
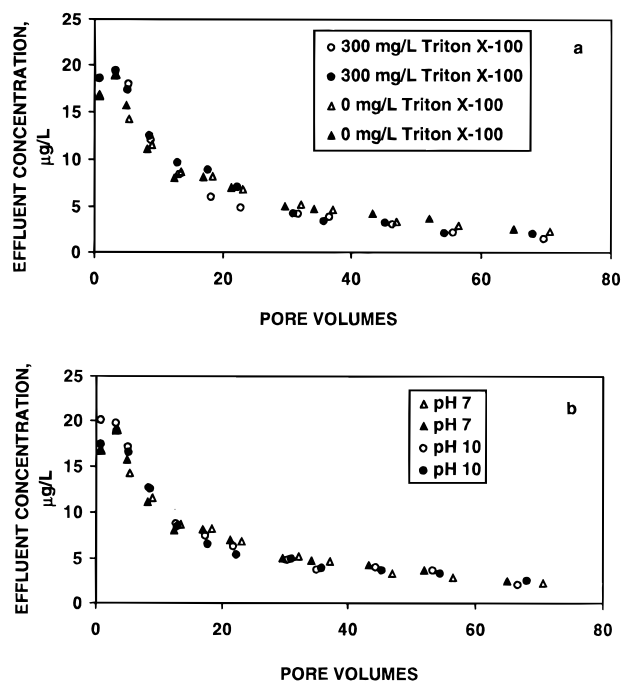

FIGURE 2. Effluent TCE concentrations from duplicate columns as a function of pore volumes: (a) effect of Triton X-100; (b) effect of pH change.
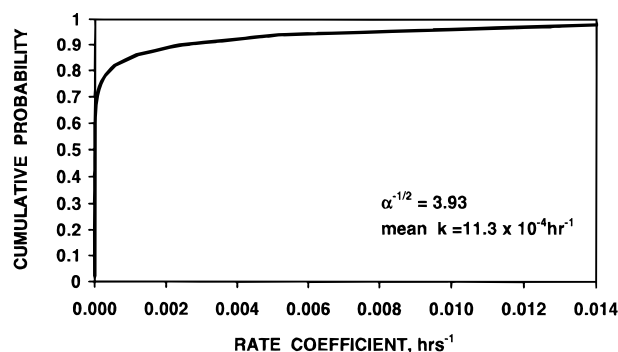

FIGURE 3. Cumulative probability distribution of rate coefficients of the soil used in the column experiment.

solution are plotted against pore volumes in Figure 2b. The data show that both surfactant flow and pH 10 buffer flow enhanced desorption during the initial 12−15 pore volumes of flow. The effluent concentrations are, however, indistinguishable for pore volumes greater than 15; both effluents show a flattening of the desorption curve at large times.

Inspection of the final TCE concentrations in the soil from all the columns (Table 3) show that the columns with 0 mg/L Triton X-100 and pH 7 have the highest final soil TCE concentrations. The addition of Triton X-100 or the increase of pH from 7 to 10 resulted in a decrease in the final sorbed TCE concentration. It should be noted, however, that the standard deviation of the data is relatively large, making the differences in residual sorbed concentrations among the columns less significant.

The cumulative probability distribution of the rate coefficients of the kinetic sites (in this case 25 sites were assumed) is given in Figure 3. It was found in our tests of the models that representing the continuum of sites by 25 discrete sites resulted in insignificant error (15). From Figure 3, it is noted that nearly 70% of the sorbed TCE exhibit very low desorption rates, nearly indistinguishable from zero. This represents a fraction that might be denoted by others as "irreversibly adsorbed", but is in fact subject to very slow desorption over a very long time period. The remaining 30% is subject to

TABLE 3. Column Flow and Soil Parameters

inflow solution	0 mg/L Triton X-100, pH 7		300 mg/L Triton X-100		pH 10 buffer	
K_d, partition coefficient (L/kg)	0.72	0.72	0.86	0.86	0.68	0.68
n, porosity	0.46	0.45	0.47	0.45	0.45	0.45
v, velocity (cm/h)	5.93	5.46	5.85	5.71	5.60	5.72
D, dispersion coefficient (cm²/h)	0.76	1.06	0.42	1.43	0.94	1.55
measured final TCE sorbed concn on soil, (μg/kg)	799.0 ± 23.3[a]	808.0 ± 41.0	777.0 ± 38.5	777.0 ± 38.5	762.3 ± 21.1	756.0 ± 29.0

[a] Standard errors of the TCE concentrations in soil.

TABLE 4. Mean Mass-Transfer Coefficients and Coefficient of Variation ($\alpha^{-1/2}$) for TCE Desorption from Soil in Packed Columns

influent solution	0 mg/L Triton X-100, pH 7		300 mg/L Triton X-100		pH 10	
mass transfer coefficient (h⁻¹)	11.14×10^{-4}	11.23×10^{-4}	14.26×10^{-4}	12.92×10^{-4}	13.42×10^{-4}	12.38×10^{-4}
$\alpha^{-1/2}$	3.808	4.06	4.191	3.986	4.29	4.153
error[a]	0.1463	0.1362	0.1646	0.1271	0.1027	0.1397
mass transfer coefficient (h⁻¹)	11.3×10^{-4}	11.0×10^{-4}	13.4×10^{-4}	12.6×10^{-4}	12.3×10^{-4}	11.74×10^{-4}
$\alpha^{-1/2}$	3.93	3.93	3.93	3.93	3.93	3.93
error	0.1474	0.1407	0.177	0.1344	0.1176	0.1506

[a] Error = [(sum of squares of deviation)/(sum of squares of data values)]^0.5.

desorption rates that lead to quantifiable desorption over time periods commonly encountered in laboratory and field remediation studies.

A variable K_d (for TCE)—in space and time—was used for the soil in the column experiment because the concentration of Triton X-100 in the column alters the K_d (Table 1). Surfactant sorption is presumably a kinetic process rather than an equilibrium process. Nevertheless, assuming equilibrium sorption and using a calibrated retardation coefficient of 49.9, an analytical transport model (CXTFIT, described in ref 27) fit of the surfactant breakthrough curves in the columns described the data fairly well. Since our model cannot handle multicomponent transport, the surfactant transport equations are solved analytically assuming equilibrium sorption to determine surfactant concentration and, thereby, K_d as a function of x and t. The K_d values are then supplied to the numerical TCE transport model. The relatively small changes in K_d values (Table 1) and the high TCE concentration gradient between the soil and aqueous phase in the columns ensure that the error introduced from using the approximate analytical solution for Triton X-100 is small.

The multi-site model is used to interpret the column runs and to calibrate the mass-transfer rate coefficients. The results from fitting the multi-site model to column data are provided in Table 4. In the two columns with no surfactant and neutral pH, the coefficients of variation (CV) are 3.808 and 4.057 (average of 3.93), and the mean mass-transfer coefficients are 11.14×10^{-3} h⁻¹ and 11.23×10^{-3} h⁻¹ (average of 11.19×10^{-4} h⁻¹). The presence of surfactant has a small effect on the coefficients of variation and increases the mean mass-transfer coefficients (to an average value of 13.6×10^{-4} h⁻¹). At the pH 10 condition, the CV changes slightly in comparison to the pH 7 condition; the mean mass-transfer coefficient increases (to an average value of 12.9×10^{-4} h⁻¹).

As is explained under the section Batch Results, to enable direct comparison of the desorption mass-transfer between columns, a set of multi-site model runs were also performed keeping the coefficient of variation constant for all the columns, with $\alpha^{-1/2} = 3.93$ (the average value of $\alpha^{-1/2}$ from the columns with 0 mg/L Triton X-100 and pH 7). The results in Table 4 indicate that addition of Triton X-100 causes approximately a 16.5% increase in the mass-transfer coefficient (average of two columns). Similarly, at pH 10 there is a 7% increase in the mass-transfer coefficient (average of two columns).

The mean rate coefficient is 1.13×10^{-3} h⁻¹. For a perspective, this value was compared with that found from

another study (9) with soil contaminated with TCE in the laboratory (for 4 weeks). The time-varying rate constant found from their study ranged between 3.0×10^{-3} h⁻¹ to 1.7×10^{-1} h⁻¹ for the 40 reactor volumes of flow. This is consistent with numerous observations that the time of contamination affects the desorption rate; the longer the contamination time, the smaller is the rate coefficient.

Contrary to our expectation, the batch mass-transfer coefficients were lower than those of the column experiments. This can be explained, in part, by extended drying of the batch soil, relative to the column soil, which may have caused conformational changes in the soil organic matter, which in turn will affect the mass transfer coefficient.

The batch and column results consistently showed that there is a small but measurable increase in mass-transfer rates in the presence of Triton X-100. Surfactants (1) sorb into the soil organic matter (SOM) causing it to swell and (2) allow water to enter the soil organic matter due to reduced surface tension—and consequently facilitate desorption. The increase in mass transfer due to increases in pH is similarly small in magnitude but consistently observed. A high pH condition deprotonates many functional groups in the soil organic matter. The increased mass-transfer coefficient at high pH is hypothesized to be a consequence of swelling (opening desorption pathways) of soil organic matter from like-charge repulsion. Further, as pH increases, K_d decreases (Table 1), which leads to a higher concentration gradient and consequently to an increased desorption rate.

Triton X-100 caused increased desorption at early times, and the mass-transfer coefficient k increased by 11.2% and 16.5% in batch studies and column studies, respectively. A buffer of pH 10 increased the mass-transfer coefficient k in batch tests by 53% and in column tests by 7%. These increases in mass transfer rate can translate into reductions in pump-and-treat remediation time. The soils used in laboratory experiments were air-dried at room temperature for 24−72 h. This process may have caused changes in the soil organic matter and altered the percentage of removable fraction of sorbed TCE. In the undisturbed field soil, therefore, increases in the mass-transfer constant in response to pH changes and surfactant addition may be different. We are currently analyzing data from a pilot-scale field test wherein low levels of Triton X-100 were injected into the TCE-contaminated aquifer at Picatinny Arsenal. Results of these analyses will be reported in the near future. In any case, for long-term field-contaminated soils, some of the TCE is very tightly bound and persists in the soil for a significant time period even for
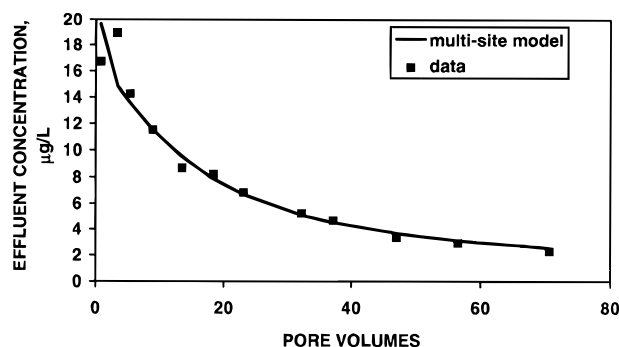
FIGURE 4. Model fits of data from one of the columns flowing water at pH 7 using the multi-site.

large desorption concentration gradients. Although the rate-limited desorption from the field soil may be problematic for complete remediation of the site, this process may contribute to relatively low aqueous-phase concentrations (possibly below regulatory limits) especially in aquifers with high flow rates.

Multi-Site Model. The ability of a multi-site sorption model to fit the data is demonstrated in a model fit to typical column data. It is evident that the multi-site model closely simulates the data over the time period of the entire experiment (Figure 4). As the faster sites reach equilibrium and the remaining slower sites are encountered, the overall mass-transfer rate is reduced. Similar model fits were obtained using the data from batch (*15*) and other column experiments. The close fit of the multi-site model indicates that the long-term contaminated soil contains a wide range of sorption sites and kinetic rate constants. This is consistent with the view that the natural soil is heterogeneous.

Acknowledgments

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